

SPECIFICATION

HAIR TREATMENT COMPRISING ACRYL/SILICONE COPOLYMER
AND

5 COSMETIC HAIR PREPARATION CONTAINING THE TREATMENT

FIELD OF THE TECHNOLOGY

This invention relates to an organopolysiloxane hair treatment agent and a hair cosmetic comprising the treatment agent. The hair treatment agent increases effects of applying hair rinse, hair conditioner or hair treatment product to the hair and improves durability of the effects.

BACKGROUND OF THE INVENTION

15 Nowadays people wash hair everyday and casually perm or color. Hair damages physically or chemically caused by the hair wash, perm or color are serious problems. For damaged hair, conditioning is necessary. As a conditioning agent, oils, cationic surfactants, proteins and hydrolysates thereof, moisturizer, higher alcohols, and emulsions are used. However, conditioning effects of the oils, cationic surfactants, proteins and hydrolysates thereof, moisturizer, higher alcohols, and emulsions are lost by a hair wash and not durable.

25 A hair treatment agent has been strongly desired which resists hair wash to maintain effects of the conditioning. As a method to maintain conditioning effects, Japanese Patent Application Laid-Open No.2001-226236 discloses a method to treat the hair with a methylhydrogenpolysiloxane. The treatment with the polysiloxane is indeed effective but not sufficient. Moreover,

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unreacted Si-H bonds remain after the treatment, which sometimes cause generation of hydrogen gas. Thus, a hair treatment agent is desired which maintains hair conditioning effect.

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DISCLOSURE OF THE INVENTION

As a result of intensive studies, the present inventors have found that the aforesaid problem of the conventional treatment agents are solved, that is, conditioning effect is improved and
10 retained, by using an acryl/silicone copolymer hair treatment agent and a hair cosmetic comprising the treatment agent.

Thus, the present provides a hair treatment agent comprising an acryl/silicone copolymer (A) having at least one hydrolyzable
15 silyl group per molecule and a hair cosmetic comprising the hair treatment agent. Preferably, the hydrolyzable silyl group is $-\text{Si}(\text{CH}_3)_{3-m}(\text{OR})_m$.

The present invention also provides a two-agent hair cosmetic
20 kit composed of a first agent comprising at least one selected from the group consisting of amino-modified silicones, amino acid-modified silicones, and carboxyl-modified silicones, and a second agent comprising the aforesaid hair treatment agent, and a three-agent hair cosmetic kit composed of the aforesaid
25 hair cosmetic kit and an amino-modified silicone.

The aforesaid cosmetic may further comprise at least one selected from an unctuous agent, water, a compound having an alcoholic hydroxyl group, a water-soluble or water-swelling polymer, a
30 surfactant, resins such as a crosslinked organopolysiloxane, and

powder and/or coloring agent.

The aforesaid cosmetic is in the form of liquid, milky lotion, cream, solid, paste, gel, multilayer, mousse, spray or stick.

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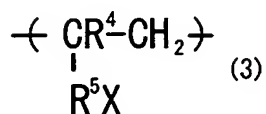
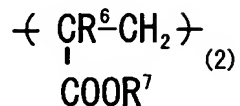
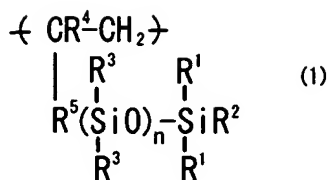
PREFERRED EMBODIMENTS OF THE INVENTION

A hair treatment agent of the present invention comprises an acryl/silicone copolymer having at least one hydrolyzable silyl group per molecule. The acryl/silicone copolymer may be of any
10 type such as a block copolymer or a graft copolymer as long as it has at least one hydrolyzable silyl group per molecule. Preferably, the acryl/silicone copolymer is an acryl/silicone graft copolymer having an acrylic polymer backbone and an organopolysiloxane polymer branch.

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Preferred hydrolyzable silyl group has a -Si-O- moiety, for example, an alkoxysilyl group or acetoxysilyl group. More preferred silyl group is represented by the formula,
-Si(CH₃)_{3-m}(OR)_m, wherein R is an alkyl, alicyclic, alkenyl, aryl,
20 or aralkyl group, preferably an alkyl or alkenyl group having 1 to 4 carbon atoms. Most preferably, R is an ethyl group. In the above formula, m is an integer of from 1 to 3. When m is 2 or 3, a plurality of R's may be different from each other. Example of preferred hydrolyzable silyl group include dimethylethoxysilyl
25 group, methyldiethoxysilyl group and triethoxysilyl group, among which triethoxysilyl group is particularly preferred.

Preferably, the acryl/silicone copolymer has the following repeating units of (1), (2) and (3).



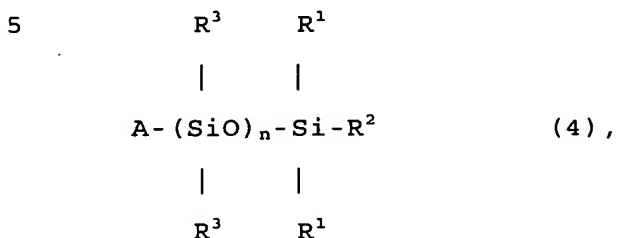
5 In the repeating units of from (1) to (3), R¹, R² and R³ may be the same with or different from each other and are selected from the group consisting of alkyl groups having 1 to 30 carbon atoms, aryl groups, aralkyl groups and fluorinated alkyl groups,
 R⁴ and R⁶ may be the same with or different from each other and
 10 are selected from the group consisting of a hydrogen atom and a methyl group,

 R⁵ may be the same with or different from each other and is an alkyleneoxycarbonyl group having 2 to 11 carbon atoms or a phenylene group,

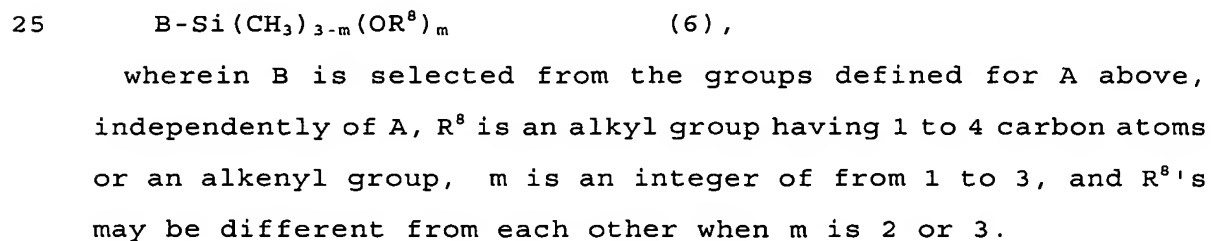
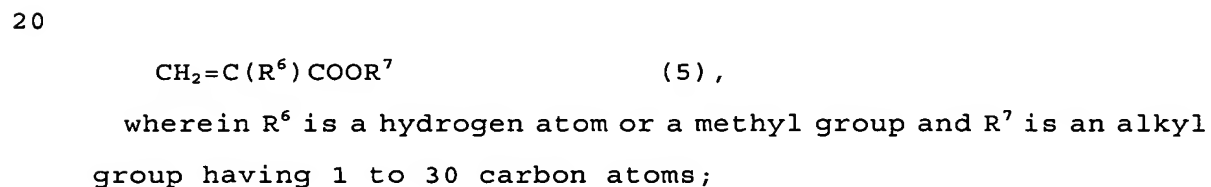
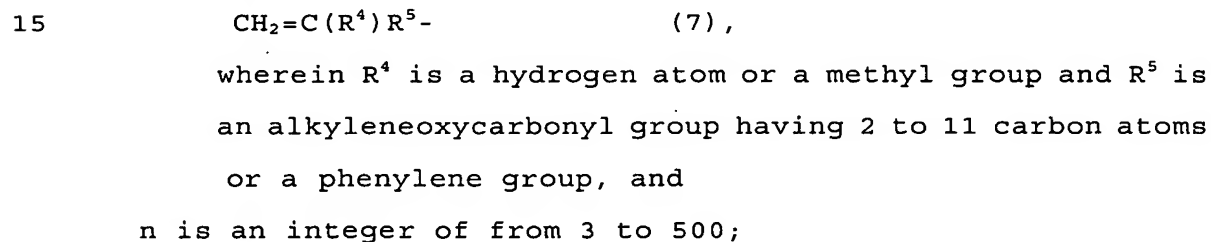
15 R⁷ is an alkyl group having 1 to 30 carbon atoms,
 X is the hydrolyzable silyl group as described above, and
 n is an integer of from 3 to 500.

 The acryl/silicone graft copolymer can be prepared by reacting
 20 an acrylic polymer with an organopolysiloxane. Preferably, for the reason of easiness in production and molecular design, so-called macromonomer method is employed by copolymerizing an organopolysiloxane represented by the following formula (4)

having a radically polymerizable group, an acrylic monomer represented by the following formula (5), and a silane compound represented by the following formula (6) having a radically polymerizable group,



wherein R^1 , R^2 and R^3 may be the same with or different from each other and are selected from the group consisting of alkyl groups having 1 to 30 carbon atoms, aryl groups, aralkyl groups and fluorinated alkyl groups, A is a radically polymerizable group represented by the following formula (7),



The organopolysiloxane compound represented by the formula (6) having a radically polymerizable group is called a silicone macromonomer. It has the radically polymerizable group at one end only. From the compound, the repeating unit (1) can be derived.

5 In the formula (4), A represents a monovalent organic group having a radically polymerizable group and is represented by the formula (7) described above. Examples of A include (meth)acryloxymethyl group, (meth)acryloxypropyl group, (meth)acryloxydecyl group, styryl group, and α -methylstyryl group, among which a

10 (meth)acryloxypropyl group is preferred.

In the formulae (1) and (4), examples of R^1 include alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl and cyclohexyl groups; aryl groups such as phenyl

15 and tolyl groups; aralkyl groups such as benzyl and phenethyl groups; and fluorinated alkyl groups such as trifluoropropyl and nonafluorobutylethyl groups. Preferably, most of R^1 are methyl groups because of good feel to the touch.

20 In the formulae (1) and (4), n is an integer of from 3 to 500, preferably from 9 to 200. An acryl/silicone copolymer with n less than the aforesaid lower limit may not provide satisfactory conditioning effect. An organopolysiloxane compound with n above the aforesaid upper limit may not copolymerize with the acrylic

25 monomer or the radically polymerizable silane compound with ease to make it difficult to obtain a desired copolymer.

From the acrylic monomer of the formula (5), the repeating unit (2) can be derived. Examples of the monomer include methyl

30 (meth)acrylate, ethyl (meth)acrylate, isopropyl (meth)acrylate,

n-butyl (meth)acrylate, tert-butyl (meth)acrylate, cyclohexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, tridecyl (meth)acrylate, stearyl (meth)acrylate, isostearyl (meth)acrylate, behenyl (meth)acrylate, and a combination thereof.

5 Preferably, methyl (meth)acrylate or a combination of any one of the aforesaid monomers which monomer can give a homopolymer having a higher glass transition temperature (T_g), and another monomer of the aforesaid monomers which gives a homopolymer having a low T_g .

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From the radically polymerizable silane compound of the formula (6), the aforesaid repeating unit (3) can be derived. Examples of the silane compound include γ -methacryloxypropyl-trimethoxysilane, γ -methacryloxypropyl-methyldimethoxysilane, 15 γ -methacryloxypropyl-dimethylmethoxysilane, γ -methacryloxypropyl-triethoxysilane, γ -methacryloxypropyl-methyldiethoxysilane, γ -methacryloxypropyl-tributhoxysilane, γ -methacryloxypropyl-isopropenoxysilane, γ -acryloxypropyl-trimethoxysilane, γ -acryloxymethyl 20 -trimethoxysilane, γ -acryloxypropyl-triethoxysilane, γ -acryloxypropylmethyl-diethoxysilane, styryltrimethoxysilane, styryltriethoxysilane, α -methylstyryltrimethoxysilane, and a mixture thereof. Preferably, γ -methacryloxypropyl-triethoxysilane is used.

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A ratio of the monomers of the formulas (4), (5) and (6) is such that the organopolysiloxane compound of the formula (4) having a radically polymerizable group is in an amount of from 1 to 97 wt%, preferably from 5 to 90 wt%, the acrylic monomer of the formula 30 (5) is in an amount of from 0 to 95 wt%, preferably from 2 to

60 wt%, and the radically polymerizable silane compound of the formula (6) is in an amount of from 1 to 10 wt%, preferably from 2 to 7 wt%, based on a total weight of the monomers. If the organopolysiloxane compound of the formula (4) is used less than the aforesaid lower limit, satisfactory effect by hair treating may not be obtained. More amount than the aforesaid upper limit of the organopolysiloxane compound may give a copolymer which does not adsorb on or react with the hair satisfactorily. If the acrylic monomer of the formula (5) is used more than the aforesaid upper limit, a copolymer having enough resistance to water may not be obtained. A less amount of the radically polymerizable silane compound of the formula (6) than the aforesaid lower limit may not give a copolymer having satisfactory reactivity with the hair. More amount than the aforesaid upper limit of the silane may give a copolymer which react among themselves in addition to with the hair. Taking the aforesaid matters into consideration, the ratio can be determined.

In addition to the aforesaid monomers, other radically polymerizable compound in an amount not to adversely affect the present invention can be copolymerized. Examples of the other radically copolymerizable monomer include carboxylic acids such as (meth)acrylic acid, fumaric acid and maleic acid; hydroxyalkyl esters such as hydroxyethyl (meth)acrylate and hydroxypropyl (meth)acrylate; acidic amides such as (meth)acrylamide; fluorinated alkyl esters such as perfluorooctylethyl (meth)acrylate, perfluorobutylethyl (meth)acrylate, styrene, acrylonitrile, vinyl acetate, vinyl pyrrolidone, polyoxyethylene mono(meth)acrylate, polyoxypropylene mono(meth)acrylate, polyoxy(ethylene/propylene) mono(meth)acrylate,

polycaprolactone mono(meth)acrylate,
tris(trimethylsiloxy)silylpropyl methacrylate, and
tris(trimethylsiloxy)silyl styrene.

5 Any method of copolymerisation can be used, for example, solution
polymerization, emulsion polymerization, suspension
polymerization, or mass polymerization, among which solution
polymerization is preferred because of uniformity of a resulting
polymer and easiness in molecular weight control. As a solvent
10 for the solution polymerization, the one in which the aforesaid
monomers and a polymer obtained can be uniformly dissolved.
Examples of the solvent include toluene, xylene, ethanol,
isopropanol, n-butanol, acetone, methyl ethyl ketone, methyl
isobutyl ketone, ethyl acetate, n-butyl acetate, isobutyl acetate,
15 diethyl ether, and tetrahydrofuran.

As a polymerization initiator, any conventionally used radical initiator may be used. Examples of the initiator include organic peroxides such as benzoylperoxide and dicumyl peroxide; and azo compounds such as azobisisobutyronitrile. A mercaptan derivative as a chain transfer agent may be used to control molecular weight of a polymer, for example, dodecyl mercaptan and mercaptopropyl trimethoxysilane. Use of a compound having a hydrolyzable group as aforementioned mercaptopropyl trimethoxysilane has an advantage that it adds a hydrolyzable silyl group to a polymer terminal. A solution of a resulting polymer can be used as such or may be diluted. Alternatively, the polymer is isolated or re-dissolved in another solvent for use as a hair treatment agent.

30 Preferably, the acryl/silicone copolymer obtained has a

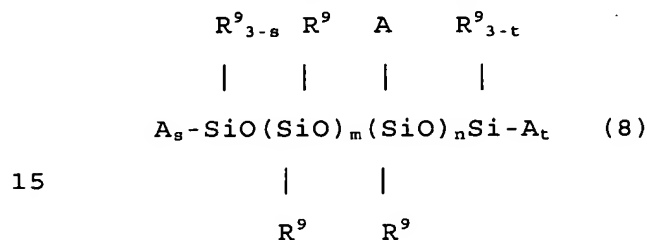
molecular weight, determined by GPC, of from 5,000 to 200,000, more preferably from 10,000 to 100,000. An acrylic-silicone copolymer having a lower molecular weight than the aforesaid lower limit may not show satisfactory effect in treating the hair. An
5 acrylic-silicone copolymer having a higher molecular weight than the aforesaid upper limit may not give a hair cosmetic having a good usability.

In the present invention, the organopolysiloxane hair
10 treatment agent (A) can be used in various ways. It can be used alone in the form of a dispersion or a solution in an organic solvent which is applied directly on the hair; it can be used in a two-agent kit composed of an aqueous or non-aqueous first agent selected from the group consisting of amino-modified
15 silicone, amino acid-modified silicone and carboxyl-modified silicone, and the present hair treatment agent (A) as a second agent; and it can be used in a three-agent kit composed of a first agent comprising an aqueous or non-aqueous amino-modified silicone, a second agent comprising the present hair treatment
20 agent (A), and a third agent comprising an aqueous or non-aqueous amino-modified silicone.

Preferably, an amino-modified silicone is used as the first agent and the present hair treatment agent is used as the non-aqueous
25 second agent. Alternatively, an amino-modified silicone is used as the first agent, the present hair treatment agent is used as the non-aqueous second agent, and an aqueous or non-aqueous amino-modified silicone is used as the third agent. In both the two-agent and the three-agent kits, it was found that conditioning
30 effect is maintained well by a synergistic effect of the

amino-modified silicone and the present hair treatment agent.

Examples of the amino-modified silicone include those having amino groups grafted to a silicone backbone, those having an amino group bonded to either one end of a silicone backbone, those having amino groups bonded to both ends of a silicone backbone, those having amino groups at both ends of a silicone backbone and an amino group grafted to the silicone backbone, and those having a silicone side chain and an amino group both grafted to a silicone backbone. Preferably, the amino-modified silicone represented by the following formula is used.



In the formula (8), A is $-R^{10}NH_2$ or $-R^{10}NHR^{11}NH_2$, wherein R^{10} and R^{11} are alkylene groups having 1 to 8 carbon atoms,

R^9 may be the same with or different from each other and is selected from the group consisting of alkyl groups having 1 to 30 carbon atoms, alicyclic groups, aryl groups, aralkyl groups, and fluorinated alkyl groups,

m and n may be the same with and different from each other and are integers of from 0 to 300, and s and t may be the same with or different from each other and are integers of from 0 to 3 with $1 \leq n+s+t$.

Examples of R^9 include alkyl group such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, and decyl groups; alicyclic groups such as cyclopentyl and cyclohexyl groups; aryl

groups such as phenyl and tolyl groups; aralkyl groups such as benzyl and phenetyl groups; and fluorinated alkyl groups such as trifluoropropyl and heptadecafluorodecyl groups, among which methyl, phenyl, and trifluoropropyl groups are preferred.

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Examples of R^{10} and R^{11} include methylene, ethylene, propylene, butylene, and pentylene groups, among which methylene, ethylene and propylene groups are preferred.

10 The present hair cosmetic may comprise various components contained in conventional cosmetics. Those components may be contained not only in one agent system composed of the component (A), but also in two- or three-agent kit as a whole, that is, the components may be incorporated in one or more of the agents
15 from first to third one. These components will be explained below.

The present cosmetic may further comprise one or more of unctuous agent (B). Any conventional unctuous agents can be used whether they are in the form of solid, semisolid or liquid. Examples of
20 the unctuous agents include natural animal or plant oils, semi-synthetic oils, hydrocarbon oils, higher alcohol oils, ester oils and conventional silicone oils.

Examples of the natural animal or plant oils and semi-synthetic
25 oils include avocado oil, linseed oil, almond oil, Chinese wax, perilla oil, olive oil, cacao butter, kapok wax, kaya oil, carnauba wax, liver oil, candellila wax, beef tallow, beef foot oil, beef bone fat, hydrogenated beef tallow, apricot kernel oil, spermaceti, hydrogenated oil, wheat germ oil, sesame oil, rice germ oil, rice
30 branoil, sugarcane wax, sasanqua oil, safflower oil, shea butter,

Chinese tung oil, cinnamon oil, jojoba wax, shellac wax, turtle oil, soybean oil, tea seed oil, tsubaki oil, evening primrose oil, corn oil, lard, rape seed oil, Japanese tung oil, rice-bran wax, germ oil, horse fat, persic oil, palm oil, palm kernel oil, 5 castor oil, hydrogenated castor oil, castor oil fatty acid methyl ester, sunflower oil, grape seed oil, bayberry wax, jojoba oil, macadamia nut oil, beeds wax, mink oil, cottonseed oil, cotton wax, Japan wax, haze kernel oil, montan wax, coconut oil, hydrogenated coconut oil, tricoconut oil fatty acid glyceride, 10 mutton-tallow, peanut oil, lanolin, liquid lanolin, reduced lanolin, lanolin alcohol, hard lanolin, lanolin acetate, lanolin fatty acid isopropyl, hexyl laurate, POE lanolin alcohol ether, POE lanolin alcohol acetate, lanolin fatty acid polyethylene glycol, POE hydrogenated lanolin alcohol ether, and egg yolk oil, 15 wherein the term "POE" stands for polyoxyethylene.

Examples of the hydrocarbon oil include ozokerite, squalane, squalene, ceresine, paraffin, paraffin wax, liquid paraffin, pristane, polyisobutylene, microcrystalline wax and Vaseline; 20 and those of a higher fatty acid which can be mixed include lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, undecylenic acid, oleic acid, linoleic acid, linolenic acid, arachidonic acid, eicosapentaenoic acid (EPA), docosahexaenoic acid (DHA), isostearic acid and 12-hydroxystearic acid.

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Examples of the higher alcohol include lauryl alcohol, myristyl alcohol, palmityl alcohol, stearyl alcohol, behenyl alcohol, hexadecyl alcohol, oleyl alcohol, isostearyl alcohol, hexyldodecanol, octyldodecanol, cetostearyl alcohol, 30 2-decyltetradecanol, cholesterol, phytosterol, POE cholesterol

ether, monostearyl glycerin ether (batyl alcohol) and monooleyl glyceryl ether (cerakyl alcohol).

Examples of the ester oil include diisobutyl adipate,
 5 2-hexyldecyl adipate, di-2-heptylundecyl adipate, N-alkylglycol
 monoisostearates, isocetyl isostearate, trimethylolpropane
 triisostearic acid ester, ethylene glycol di-2-ethylhexanoic acid
 ester, cetyl 2-ethylhexanoate, trimethylolpropane
 tri-2-ethylhexanoic acid ester, pentaerythritol
 10 tetra-2-ethylhexanoic acid ester, cetyl octanoate, octyldodecyl
 gum ester, oleyl oleate, octyldodecyl oleate, decyl oleate,
 neopentyl glycol dicapric acid ester, triethyl citrate,
 2-ethylhexyl cinnamate, amyl acetate, ethyl acetate, butyl
 acetate, isocetyl stearate, butyl stearate, diisopropyl sebacate,
 15 di-2-ethylhexyl sebacate, cetyl lactate, myristyl lactate,
 isopropyl palmitate, 2-ethylhexyl palmitate, 2-hexyldecyl
 palmitate, 2-heptylundecyl palmitate, cholesteryl
 12-hydroxystearate, dipentaerythritol fatty acid esters,
 isopropyl myristate, octyldodecyl myristate, 2-hexyldecyl
 20 myristate, myristyl myristate, hexyldecyl dimethylcanoate,
 ethyl laurate, hexyl laurate, N-lauroyl-L-glutaminic acid
 2-octyldodecyl ester and diisostearyl malic acid; and examples
 of glyceride oil which can be mixed therein include acetoglyceride,
 triisooctanoic acid glycride, triisostearic acid glyceride,
 25 triisopalmitic acid glyceride, tri-2-ethylhexanoic acid
 glyceride, monostearic acid glyceride, di-2-heptylundecanoic
 acid glyceride, trimyristic acid glyceride and myristic acid
 isostearic acid diglyceride.

30 Examples of the conventional silicone oil include

organopolysiloxanes having a viscosity of from a low value to a high value, preferably from 0.65 to 1,000,000mm²/s, such as dimethylpolysiloxane, methylphenylpolysiloxane, methylhydrogenpolysiloxane and a copolymer of dimethylsiloxane and methylphenylsiloxane; cyclic siloxanes, such as octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, tetramethyl-tetrahydrogencyclotetrasiloxane; silicone rubbers, such as gummy dimethylpolysiloxanes having high polymerization degrees and gummy dimethylsiloxane-methylphenylsiloxane copolymers having high polymerization degrees; and cyclosiloxane solutions of silicone rubber, trimethylsiloxysilicate, cyclosiloxane solutions of trimethylsiloxysilicate, higher alkoxy-modified silicones such as stearoxysilicone, higher fatty acid-modified silicones, alkyl-modified silicones, siliconols, fluorine-modified silicones, and solutions of silicone resins in a cyclic siloxane.

Examples of fluorine-containing oil include perfluoropolyether, perfluorodecalin and perfluorooctane.

A content of these unctuous agents (B) may vary depending on the form of the cosmetic and range from 0.01 to 99 wt% based on a total weight of the cosmetic.

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The present hair cosmetic may further comprise (C) water according to a purpose of the cosmetic. A content of water (C) may vary depending on the form of the cosmetic and ranges from 0.01 to 99 wt% based on a total weight of the cosmetic.

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The present cosmetic may further comprise one or more of a compound (D) having at least one alcoholic hydroxyl group per molecule, depending on a purposes of the cosmetic. Examples of the compound (D) include lower alcohols, such as ethanol and isopropanol; sugar alcohols, such as sorbitol and maltose; sterols, such as cholesterol, sitosterol, phytosterol and lanosterol; and polyhydric alcohols such as butylene glycols, propylene glycols, dibutylene glycols, and pentylene glycols. The compound (D) may be incorporated in the cosmetic in an amount of from 0.1 to 98 wt% based on a total weight of the cosmetic.

The present cosmetic may further comprise one or more of a water-soluble or water-swellig polymer (E). Examples of the water-soluble or water-swellig polymer include plant origin polymers, such as gum arabic, tragacanth, galactan, carob gum, guar gum, karaya gum, carrageenan, pectin, agar, quince seed, starch (rice, corn, potato, wheat), alge colloid, tranto gum and locust beangum; microbial polymers, such as xanthangum, dextran, succinoglucan and pullulan; animal polymers, such as collagen, casein, albumin and gelatin; starch polymers, such as carboxymethyl starch and methylhydroxypropyl starch; cellulose polymers, such as methyl cellulose, ethyl cellulose, methylhydroxypropyl cellulose, carboxymethyl cellulose, hydroxymethyl cellulose, hydroxypropyl cellulose, nitrocellulose, sodium cellulose sulfate, sodium carboxymethylcellulose, crystalline cellulose and powdery cellulose; alginic acid polymers, such as sodium alginate and propylene glycol ester of alginic acid; vinyl polymers, such as polyvinyl methyl ether and carboxyvinyl polymer; polyoxyethylene polymers; polyoxyethylene-polyoxypropylene copolymers; acrylic

polymers, such as sodium polyacrylate, polyethylacrylate and polyacrylamide; other synthetic water-soluble polymers, such as polyethyleneimines and cationic polymers; and inorganic water-soluble polymers, such as bentonite, aluminum magnesium silicate, montmorillonite, beidellite, nontronite, saponite, hectorite and silicic acid anhydride. The water-soluble polymer encompasses film-forming agents, such as polyvinyl alcohol and polyvinyl pyrrolidine, are also included. It may be incorporated in the cosmetic in an amount of from 0.1 to 25 wt% based on a total weight of the cosmetic.

The present hair cosmetic may further comprise one or more of a surfactant (F) according to a purpose of the cosmetic. Examples of the surfactant include anionic, cationic, nonionic and amphoteric surfactants and are not limited to a particular one. Any surfactant can be used so long as it is used in ordinary cosmetics.

Examples of the anionic surfactant include fatty acid soap, such as sodium stearate or triethanolamine palmitate; alkyl ether carboxylic acids and salts thereof; salts of amino acid-fatty acid condensates; alkanesulfonates; alkenesulfonates; sulfonated fatty acid esters; sulfonated fatty acid amides; sulfonates of formaldehyde condensate type; alkylsulfates; higher secondary alcohol sulfates; alkyl and aryl ether sulfates; fatty acid ether sulfates, fatty acid alkylolamide sulfates; ether sulfates, such as Turkey red oil; alkyl phosphates; ether phosphates; alkyl aryl ether phosphates; amide phosphates; and active agents of N-acylamino acid type.

Examples of the cationic surfactant include amine salts, such as alkylamine salts, polyamines and aminoalcohol fatty acid derivatives, quaternary alkylammonium salts, quaternary arylammonium salts, pyridinium salts and imidazolium salts.

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Examples of the nonionic surfactant include sorbitan fatty acid esters, glycerin fatty acid esters, polyglycerin fatty acid esters, propylene glycol fatty acid esters, polyethylene glycol fatty acid esters, sucrose fatty acid esters, polyoxyethylene alkyl
 10 ethers, polyoxypropylene alkyl ethers, polyoxyethylene alkyl phenylethers, polyoxyethylene fatty acid esters, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene sorbitol fatty acid esters, polyoxyethylene glycerin fatty acid esters, polyoxyethylene propylene glycol fatty acid esters,
 15 polyoxyethylene castor oil, polyoxyethylene hydrogenated castor oil, polyoxyethylene phytostanol ether, polyoxyethylene phytosterol ether, polyoxyethylene cholestanol ether, polyoxyethylene cholesteryl ether, linear or branched polyoxyalkylene-modified organopolysiloxanes, linear or
 20 branched organopolysiloxanes modified with both polyoxyalkylene and alkyl groups, linear or branched polyglycerin-modified organopolysiloxanes, alkanolamides, sugar ethers and sugar amides; and examples of a usable amphoteric surfactant include
 25 betaine, aminocarboxylates and imidazoline derivatives. The surfactant may be incorporated in the cosmetic preferably in an amount of from 0.1 to 20 wt%, particularly 0.2 to 10 wt%, based on a total weight of the cosmetic.

The present cosmetic may further comprise one or more of a
 30 crosslinked organopolysiloxane (G), depending on a purpose of

the cosmetic. The crosslinked organopolysiloxane preferably has been swelled with a silicone having a low viscosity of from 0.65 to 10.0 mm²/sec (25°C) in an amount larger than a weight of the organopolysiloxane (G). Preferred crosslinked organopolysiloxane is a reaction product of an organopolysiloxane having at least two alkenyl groups per molecule and an organohydrogenpolysiloxane having a Si-H bond. The crosslinked organopolysiloxane may have at least one moiety selected from polyoxyalkylene, polyglycerol, alkyl, alkenyl, aryl and fluoroalkyl moieties. The crosslinked organopolysiloxanes may be incorporated in the cosmetic preferably in an amount of from 0.1 to 50 wt%, more preferably from 1 to 30 wt%, based on a total weight of the cosmetic.

The present cosmetic may further comprise one or more of a conventional silicone resin (H). Preferred silicone resin is an acryl/silicone graft or block copolymer without having a hydrolyzable silyl group. Use may be made of an acryl/silicone resin having no hydrolysable silyl group and at least one moiety selected from the group consisting of pyrrolidone moieties, long-chain alkyl moieties, polyoxyalkylene moieties, fluoroalkyl moieties and carboxylic acid moieties.

Preferably, this silicone resin is a silicone compound having a network structure represented as MQ, MDQ, MT, MDT, or MDTQ. Use may be made of a silicone network compound having at least one moiety selected from the group consisting of pyrrolidone, long-chain alkyl, polyoxyalkylene, fluoroalkyl, and amino moieties.

The silicone resin may be incorporated in the cosmetic preferably

in an amount of from 0.1 to 20 wt%, more preferably from 1 to 10 wt%.

The present cosmetic may further comprise one or more of powder
5 and/or coloring agent (I) depending on a purpose of the cosmetic.
Any powder conventionally used in cosmetics can be used
irrespective of its form, for example, spherical, acicular or
tabular; its size, for example, fume state, fine grain or pigment
grade; and its structure, for example, porous or nonporous.
10 Examples include inorganic powder, organic powder, metal salt
surfactant powder, colored pigments, pearl pigments, metallic
powder pigments and natural pigments.

Examples of the inorganic powder include titanium dioxide,
15 zirconium oxide, zinc oxide, cerium oxide, magnesium oxide, barium
sulfate, calcium sulfate, magnesium sulfate, calcium carbonate,
magnesium carbonate, talc, mica, kaolin, sericite, muscovite,
synthetic mica, phlogopite, ruby mica, biotite, lipidolite,
silicic acid, silicic acid anhydride, aluminum silicate,
20 magnesium silicate, aluminum magnesium silicate, calcium silicate,
barium silicate, strontium silicate, metal salts of tungstic acid,
hydroxyapatite, vermiculite, haidilite, bentonite,
montmorillonite, hectorite, zeolite, ceramics powder, calcium
secondary phosphate, alumina, aluminum hydroxide, boron nitride
25 and silica.

Examples of the organic powder include polyamide powder,
polyester powder, polyethylene powder, polypropylene powder,
polystyrene powder, polyurethane powder, benzoguanamine powder,
30 polymethylbenzoguanamine powder, polytetrafluoroethylene powder,

polymethylmethacrylate powder, cellulose powder, silk powder, nylon powder such as 12-nylon powder or 6-nylon powder, crosslinked dimethylsilicone fine powder, polymethylsilsesquioxane fine powder, powder of crosslinked silicone composite with
 5 polymethylsilsesquioxane bonded to the silicone, styrene-acrylic acid copolymer powder, divinylbenzene-styrene copolymer powder, vinyl resin powder, urea resin powder, phenol resin powder, fluoro resin powder, silicone resin powder, acrylic resin powder, melamine resin powder, epoxy resin powder,
 10 polycarbonate resin powder, microcrystalline fiber powder, starch powder and lauroyl lysine powder.

Examples of the metal salt surfactant powder (metal soap powder) include powders of zinc stearate, aluminum stearate, calcium
 15 stearate, magnesium stearate, zinc myristate, magnesium myristate, zinc cetylphosphate, calcium cetylphosphate and zinc sodium cetylphosphate.

Examples of the colored pigment include red pigments, such as
 20 iron oxide, iron hydroxide and iron titanate; inorganic brown pigments, such as γ -iron oxide; inorganic yellow pigments, such as iron oxide yellow and loess; inorganic black pigments, such as iron oxide black and carbon black; inorganic violet pigments, such as manganese violet and cobalt violet; inorganic green
 25 pigments, such as chromium hydroxide, chromium oxide, cobalt oxide and cobalt titanate; inorganic blue pigments, such as Prussian blue and ultramarine blue; lakes of tar pigments; lakes of natural dyes; and a composite powder of two or more of above.

30 Examples of the pearl pigment include titanium oxide-coated mica,

bismuth oxychloride, titanium oxide-coated bismuth oxychloride, titanium oxide-coated talc, fish scales, and titanium oxide-coated colored mica. Examples of the metallic powder pigment include aluminum powder, copper powder and stainless powder.

5 Examples of the tar pigment include Red No. 3, Red No. 104, Red No. 106, Red No. 201, Red No. 202, Red No. 204, Red No. 205, Red No. 220, Red No. 226, Red No. 227, Red No. 228, Red No. 230, Red No. 401, Red No. 505, Yellow No. 4, Yellow No. 5, Yellow No. 202, Yellow No. 203, Yellow No. 204, Yellow No. 401, Blue No. 1, Blue

10 No. 2, Blue No. 201, Blue No. 404, Green No. 3, Green No. 201, Green No. 204, Green No. 205, Orange No. 201, Orange No. 203, Orange No. 204, Orange No. 206 and Orange No. 207; and examples of the natural pigment include powders of carminic acid, laccaic acid, carthamin, bradilin and crocin.

15

The powder may be used as in a composite form or may be treated with a commonly used oil, silicone oil, fluorocompound, or surfactant. The powder may be used as a mixture of two or more thereof, if desired. The powder is incorporated in the cosmetic

20 preferably in an amount of from 0.1 to 99 wt% based on a total weight of the cosmetic.

To the present cosmetic may further comprise ingredients used in general cosmetics such as oil-soluble gelling agents, clay

25 minerals modified with organic compounds, resins, ultraviolet absorbents or scattering material, moisturizing agents, antiseptics, antimicrobial agents, perfume, salts, antioxidants, pH regulators, chelating agents, refrigerant, anti-inflammatory agents, skin beautifying components (a skin whitener, a cell

30 activator, a rough dry skin improver, a blood circulation promoter,

a skin astringent and an anti-seborrheic agent), vitamins, amino acids, nucleic acids, hormones and clathrate compounds, and polymers for hair setting, in an amount not to have adverse influences on the effects of the present invention.

5

Examples of the oil-soluble gelling agent include metal soaps, such as aluminum stearate, magnesium stearate and zinc myristate; amino acid derivatives, such as N-lauroyl-L-glutamic acid and α, γ -di-n-butylamine; dextrin fatty acid esters, such as dextrin palmitic acid ester, dextrin stearic acid ester and dextrin 2-ethylhexaminic acid palmitic acid ester; sucrose fatty acid esters, such as sucrose palmitic acid ester and sucrose stearic acid ester; benzylidene derivatives of sorbitol, such as monobenzylidene sorbitol and dibenzylidene sorbitol; and clay minerals modified with organic compounds, such as dimethylbenzyl dodecyl ammonium montmorillonite clay and dimethyldioctadecyl ammonium montmorillonite clay.

Examples of the ultraviolet light absorbent include those of benzoic acid type, such as p-aminobenzoic acid; those of anthranilic acid type, such as methyl anthranilate; those of salicylic acid type, such as methyl salicylate; those of succinic acid type, such as octyl p-methoxysuccinate; those of benzophenone type, such as 2,4-dihydroxybenzophenone; those of urocanic acid type, such as ethyl urocanate; and those of dibenzoylmethane type, such as 4-t-butyl-4'-methoxydibenzoylmethane. Examples of ultraviolet scattering material include titanium oxide fine powder, fine powder of titanium oxide containing iron, zinc oxide fine powder, cerium oxide fine powder, a composed powder of two or more of these and powder which absorbs and scatters ultraviolet.

Examples of the moisturizing agent include glycerin, sorbitol, propylene glycol, dipropylene glycol, 1,3-butylene glycol, glucose, xylitol, maltitol, polyethyleneglycol, hyaluronomic acid, chondroitin sulfuric acid, pyrrolidone carboxylic acid, polyoxyethylene glycoside, and polyoxypropylene methylglycoside.

Examples of the antiseptic agent include alkyl p-hydroxybenzoates, benzoic acid, sodium benzoate, sorbic acid, potassium sorbate and phenoxyethanol; and those of an antimicrobial agent which can be added include benzoic acid, salicylic acid, carbolic acid, sorbic acid, alkyl p-hydroxybenzoates, p-chlorometacresol, hexachlorophene, benzalkonium chloride, chlorhexidine chloride, trichlorocarbanilide, photosensitizer and phenoxyethanol.

Examples of the antioxidant include tocopherol, butylhydroxyanisole, dibutylhydroxytoluene and phytic acid; those of a pH regulator which can be added include lactic acid, citric acid, glycolic acid, succinic acid, tartaric acid, dl-malic acid, potassium carbonate, sodium hydrogen carbonate and ammonium hydrogen carbonate; those of a chelating agent which can be added include alanine, sodium ethylenediaminetetraacetate, sodium polyphosphate, sodium metaphosphate and phosphoric acid; those of a refrigerant which can be added include L-menthol and camphor; and those of an anti-inflammatory agent which can be added include allantoin, glycyrrhizin and salts thereof, glycyrrhetinic acid and stearyl glycyrrhetinate, tranexamic acid and azulene.

Examples of the skin-beautifying component include whitening agents, such as placenta extract, arbutin, glutathione and Yukinoshita extract; cell activators, such as royal jelly, photosensitizer, cholesterol derivatives and calf blood extract; 5 rough dry skin improvers; blood circulation improvers, such as nonylic acid vanillyl amide, benzyl nicotinate, β -butoxyethyl nicotinate, capsaicin, zingerone, cantharistincture, ichtammol, caffeine, tannic acid, α -borneol, tocopheryl nicotinate, inositol hexanicotinate, cyclandelate, cinnarizine, tolazoline, acetyl 10 choline, verapamil, cepharanthin and γ -oryzanol; skin astringents, such as zinc oxide and tannic acid; and anti-seborrheic agents, such as sulfur and thianthol.

Examples of the vitamin include vitamin A, such as vitamin A 15 oil, retinol, retinyl acetate and retinyl palmitate; vitamin B, including vitamin B2 such as riboflavin, riboflavin butyrate and flavin adenine nucleotide, vitamin B6 such as pyridoxine hydrochloride, pyridoxine dioctanoate and pyridoxine tripalmitate, vitamin B12 and its derivatives, and vitamin B15 20 and its derivatives; vitamin C, such as L-ascorbic acid, L-ascorbic acid dipalmitic ester, sodium (L-ascorbic acid) -2-sulfate and dipotassium L-ascorbic acid diphosphate; vitamin D, such as ergocalciferol and cholecalciferol; vitamin E, such as α -tocopherol, β -tocopherol, γ -tocopherol, dl- α -tocopheryl 25 acetate, dl- α -tocopheryl nicotinate and dl- α -tocopheryl succinate; vitamin H; vitamin P; nicotinic acids, such as nicotinic acid, benzyl nicotinate and nicotinic acid amide; pantothenic acids, such as calcium pantothenate, D-pantothenyl alcohol, pantothenyl ethyl ether and acetylpantothenyl ethyl ether; and 30 biotin.

Examples of the amino acid include glycine, valine, leucine, isoleucine, serine, threonine, phenylalanine, arginine, lysine, aspartic acid, aspartic acid, glutamic acid, cystine, cysteine, methionine, and tryptophan; those of a nucleic acid which can be added include deoxyribonucleic acid; and those of hormone which can be added include estradiol and ethenyl estradiol.

Examples of the polymer for hair setting include amphoteric, anionic, cationic, and nonionic polymers, such as polymers of polyvinyl pyrrolidone type such as polyvinyl pyrrolidone, vinyl pyrrolidone /vinyl acetate copolymers; acidic polymers of vinyl acetate ether type such as methyl vinyl ether / maleic acid anhydride alkyl half ester copolymer; polymers of acidic polyvinyl acetate type such as vinyl acetate / crotonic acid copolymer; acidic acrylic polymers such as (meth)acrylic acid / alkyl (meth)acrylate copolymer, (meth)acrylic acid / alkyl (meth)acrylate / alkyl acrylic amide copolymer, and amphoteric acrylic polymer such as N-methacryloylethyl-N,N-dimethylammonium alpha-N-methylcarboxybetaine / alkylmethacrylate copolymer, hydroxypropyl (meth)acrylate/butylaminoethyl methacrylate / octyl amide of acrylic acid copolymer. Use is also made of naturally occurring polymers such as cellulose or derivatives thereof, keratin, collagen and derivatives thereof.

25

The present hair cosmetic may be in the form of liquid, milky lotion, cream, solid, paste, gel, multilayer, mousse, spray or stick.

EXAMPLES

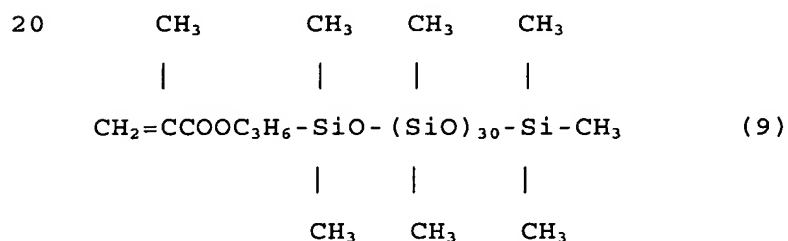
The present invention will be explained in detail with reference

30

to Examples, but not limited thereto. In the following, "%" means % by weight unless otherwise specified.

Synthesis Example 1

5 In a glass flask provided with a stirrer, a thermometer and a reflux condenser, 50 wt% of the radically polymerizable organopolysiloxane of the following formula (9), 5 wt% of methyl methacrylate, 40 wt% of stearyl methacrylate, 5 wt% of γ -methacryloxypropyl-trimethoxysilane, toluene in the same
10 weight as a total weight of the aforesaid monomers, and azobisisobutyronitrile in an amount of 1% by weight of a total weight of the monomers and toluene were placed and subjected to polymerization by heating under nitrogen stream at 100 °C for 10 hours. Then, toluene was distilled off at a reduced pressure.
15 An acryl/silicone graft copolymer for the hair thus obtained was light yellow solid having a melting point of 30°C and a weight average molecular weight, determined by GPC, of 42,000 in polystyrene equivalent.



Synthesis Example 2

An acryl/silicone graft copolymer was prepared as in Example 1 by copolymerizing 50 wt% of the radically polymerizable organopolysiloxane of the above formula (9), 30 wt% of methyl
30 methacrylate, 7.5 wt% of butyl methacrylate, 7.5 wt% of 2-ethyl

hexyl acrylate and 5 wt% of γ -methacryloxypropyl-triethoxysilane. The copolymer obtained was transparent light yellow resin having a softening point of 93 °C and a weight average molecular weight, determined by GPC, of 55,000 in polystyrene equivalent.

5

Synthesis Example 3

An acryl/silicone graft copolymer was prepared as in Example 1 by copolymerizing 90 wt% of the radically polymerizable organopolysiloxane of the following formula (10), 50 wt% of methyl methacrylate, and 5 wt% of γ -methacryloxypropyl-triethoxysilane. The copolymer for the hair obtained was colorless transparent liquid having a viscosity at 25 °C of 270 mm²/sec, a specific gravity of 0.981, a refractive index of 1.4152 and a weight average molecular weight, determined by GPC, of 11,000 in polystyrene equivalent.

15

Example 1. Hair spray (one-agent type)

Components	wt %
1. Synthesis Example 2	5.0
2. Ethanol	95.0

The components described above were mixed. The mixture was packed in a spray container to prepare a hair spray. The hair spray obtained was tested by five female panelists and rated according to the following criteria by comparing the hair to which the hair spray was applied with the reference hair which was not applied with the hair spray in terms of easiness to comb, moisturized feel, softness, and gloss.

20

25

Mark	Easiness to comb	Moisturized feel, softness, and gloss
5	Much easier	Significant
4	A little easier	A little more than the reference level
3	Reference level	Reference level
2	A little difficult than the reference	A little less than the reference level
1	Much difficult	None

The marks were averaged and used for evaluation according to
5 the criteria shown below.

Evaluation according to an averaged mark:

Averaged mark	
4.5 or higher	A
3.5 to below 4.5	B
2.5 to below 3.5	C
1.5 to below 2.5	D
below 1.5	E

Comparative Example 1

10 A hair spray was prepared as in Example 1 except that a methylhydrogenpolysiloxane was used in place of the organopolysiloxane prepared in Synthetic Example 2.

Results of Example 1 and Comparative Example 1 are as shown in

Table 1 below.

Table 1

	Example 1	Comparative Example 1
Easiness to comb	A	A
Moisturized feel	A	B
Softness	A	A
Gloss	A	B

As is evident from Table 1, the hair treated with the hair spray
5 of the present invention was easy to comb, moisturized, soft and
glossy compared with the hair treated with
methylhydrogenpolysiloxane.

Examples 2-5, Comparative Examples 2-4

10 Hair treatment agents each having the formulation shown in Table
2 were prepared.

Table 2

First agent		Ex.*3.2	Ex.3	Ex.4	Ex.5	Comp.Ex.*4.2	Comp.Ex.3	Comp.Ex.4
1	Amino-modified silicone*1	5	5	5	-	5	5	5
2	Cetanol	8	8	8	-	8	8	8
3	Stearyl trimethyl ammonium chloride	3.5	3.5	3.5	-	3.5	3.5	3.5
4	Glycerin	5	5	5	-	5	5	5
5	Purified water	78.5	78.5	78.5	-	78.5	78.5	78.5
Second agent								
1	Synthesis example 1	6	-	-	6	-	-	-
2	Synthesis example 3	-	6	-	-	-	-	-
3	Synthesis example 4	-	-	6	-	-	-	-
4	Methylhydrogen polysiloxane	-	-	-	-	6	6	-
5	Ethanol	94	94	94	94	94	94	100
Third agent								
1	Amino-modified silicone*1	-	-	2	-	-	2	-
2	Highly polymerized methylpoly-siloxane solution*2	-	-	5	-	-	5	-
3	Cetanol	-	-	8	-	-	8	-
4	Stearyl trimethyl ammonium chloride	-	-	3.5	-	-	3.5	-
5	Glycerin	-	-	3	-	-	3	-
6	Purified water	-	-	78.5	-	-	78.5	100

*1 Amino-modified silicone :KF-8005, ex Shin-Etsu Chemical Co.,Ltd.

*2 Solution of a Highly polymerized methylpolysiloxane: KF-9013,
ex Shin-Etsu Chemical Co., Ltd.

*3 "Ex." stands for Example.

*4 "Comp.Ex." stands for Comparative Example.

Each hair treatment agent was evaluated using hair bundles for testing.

The hair bundle for testing was a bundle of ordinary hair with
5 a length of 20 cm and a total weight of 6.0 g which had been shampooed
and breached with a breaching agent.

In Examples 2 and 3, the hair bundle was coated with one gram
of a first agent followed by washing with water, and then coated
10 with one gram of a second agent followed by drying; in Example
4, the hair bundle was treated with a first agent and then a second
agent as described above, and then coated with one gram of a third
agent; and in Example 5, the hair bundle was washed and then coated
with one gram of a second agent. Each of thus treated hair bundle
15 was processed under the conventional conditions by treating with
a conventional hair treatment product, rinsing and drying.

Subsequently, the process consisting of shampooing, hair
treatment with a treatment product and drying was repeated 20
20 times consecutively.

The hair bundles immediately after treated with the present hair
treatment agent and those after 20 cycles of the processing were
compared with as ordinary hair being a reference in easiness to
25 comb, moisturized feel, softness, and gloss. Results are as shown
in the following Table.

Table 3

Immediately after treatment	Example 2	Example 3	Example 4	Example 5	Comp.Ex.2	Comp.Ex.3	Comp.Ex.4
Easiness to comb	A	A	A	A	B	A	B
Moisturized feel	A	A	A	A	B	B	B
Softness	A	A	A	A	A	A	B
Gloss	A	A	A	A	B	A	B
After 20-cycle processing							
Easiness to comb	A	A	A	B	D	C	D
Moisturized feel	A	A	A	A	D	B	D
Softness	A	A	A	A	D	B	D
Gloss	A	A	A	B	D	C	D

As shown in Table 3, compared with the hair cosmetic of Comparative Examples, the hair treatment cosmetics of the present invention were superior in all the aspects, i.e., easiness to comb, moisturizing effect, softening effect and gloss, indicating improvement in durability of hair treatment applied to the hair.

In Examples 2 to 4, the hair after 20-cycle processing showed the same result as that of the hair immediately after treated, indicating excellent resistance to shampooing. Especially, Examples 2 and 5, wherein the present treatment agent is used together with the amino-modified silicone, durable coating film on the hair was formed to maintain smoothness in combing and gloss, compared with Comparative Example 4. Although, the effect was demonstrated by using amino-modified silicones, the same effect is attained with amino acid-modified silicones and carboxyl-modified silicones hair treatment agent.